Further Developments in High-Temperature Natural Gas Fuel Cells

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INTRODUCTION

Fuel cell research at the Institute of Gas Technology began in 1959. Using the work done by Broers (2) on the molten carbonate high-temperature fuel cell as a starting point, IGT has concentrated a large portion of its effort on further development of this system from both a fundamental and an engineering viewpoint. Background material and earlier work from this laboratory, through 1960, have been described elsewhere (11).

During the past 2 years the research and development effort of IGT on a natural gas operated, molten carbonate fuel cell system has been in five areas:

- Electrode evaluation and design
- Paste electrolyte development
- Natural gas reforming
- Battery design and scaleup
- Economic evaluation

In this paper the results in these five areas are summarized. All five areas are strongly interrelated and interdependent, and each combination of electrode, electrolyte, reformer, and battery design gives rise to different fundamental requirements for one or more of the individual components. Any given design will affect the economics of the fuel cell system.

In his economic analysis of domestic fuel cell systems, von Fredersdorff (12) has indicated some of the limitations on fuel cell hardware costs. It has been an important part of this research to establish the feasibility of economic hardware for natural gas operation.

ELECTRODE EVALUATION AND DESIGN

Almost all fuel cell electrodes must possess the same general characteristics of high electrocatalytic activity, good mass transport properties, and long-term physical and chemical stability. In the high-temperature molten carbonate system, the activity criterion is alleviated by the elevated operating temperatures, and the mass transfer problems are not unlike those associated with other types of fuel cells. However, the stability problems are in many respects unique because of the properties of the molten carbonate electrolyte and the operating temperatures.

At IGT a number of different types of electrodes have been studied from both a structural and chemical viewpoint in the last 2 years. Metal foil, thin film, sintered powder, and sintered fiber structures have been explored. Materials used in these investigations have been platinum, nickel, silver, palladium and alloys of silver and palladium.

Metal Foil Electrodes

Hydrogen permeable metal foils have been used for some time in conjunc-

tion with commercial hydrogen purification processes, and much technical literature on these materials is available (4,7). IGT was attracted to the concept of a metal foil anode early in its program as an expedient means for solving two problems associated with the molten carbonate fuel cell, electrode flooding and corrosion. The first foils studied were alloys of palladium and silver, of which typical performance is shown in Figure 1. Complete details of the IGT palladium foil fuel cell have been published (9). Since the anode in this cell is not permeable to the reaction products, the mass transport processes are very different from those associated with more conventional molten carbonate fuel cells. A variety of experiments indicated that the overall anode reaction is strongly limited by the diffusion of reaction products, carbon dioxide and water, away from the electrode. The fact that diffusion of hydrogen through the foil did not appear to be limiting led to experiments with pure palladium foils of poorer hydrogen diffusion characteristics. Somewhat better cell performance was observed (Figure 1), although a direct comparison could not be made, because improvements in other cell components were incorporated at the same time.

Silver-palladium diffusion foil electrodes have operated continuously under 25 ma. per sq. cm. load for over 7 months without apparent damage to the anodes. Unfortunately, these palladium diffusion foil electrodes are too expensive for gas industry use. At present other, less expensive, hydrogen permeable foil electrode materials are being investigated.

Thin Film Electrodes

The use of metal film electrodes is economically attractive, especially in those cases where noble metals are needed. With semisolid electrolyte molten carbonate fuel cells it is possible to use the electrolyte, which at suboperating temperature is a solid, as the support for applying the thin film. Electrodes were applied by vacuum deposition and simple painting techniques. In the latter, the metal to be deposited exists as a finely dispersed particle in an organic binder. All solutions used for the process were commercially available.

The first experiments were directed toward development of a thin film silver cathode. The major anticipated difficulty in this instance was the dissolution of the silver in the electrolyte. Douglas (5), Broers (3) and Janz (8) have discussed this problem. Silver film electrodes (0.001 cm. thick) prepared from commercial silver paints have performed over 4000 hours at 600°C. without apparent loss in performance although some dissolution of silver in the electrolyte did occur. The relatively long lifetime is attributed to the fact that the cells were operated at lower temperatures than those used in the work of others and were continuously under load; the oxygen electrode is always cathodically polarized, suppressing the dissolution reaction. Moreover, cathodes were not physically flooded to any significant extent.

The successes with the silver film cathodes led to experimentation with other metals in an effort to develop a similar type of anode structure. Little success was achieved in this area primarily because of electrode flooding. Results of various experiments are summarized in Table I. The best results were achieved with vacuum-deposited palladium; however, the cell lifetimes obtained were only about 300 hours.

Since performance decreases with load, anode flooding could have been caused either by carbonate ion transport, or by drag forces exerted on the electrolyte by the escaping reaction products. However, the reaction products do not cause cathode flooding when they are forced to escape through a film cathode (by using a foil anode, which is impermeable to the reaction products). Hence, flooding must be associated with the directional character of ionic transport phenomena. A more detailed investigation of these effects is now in progress.

Sintered Metal Electrodes

Two types of sintered metal electrodes have been investigated: 1) conventional nickel and silver powder electrodes available from Clevite Corporation; and 2) nickel and palladium fiber metal electrodes obtained from Armour Research Foundation of Illinois Institute of Technology. Early in the study, it was observed that similar performances were obtained from bulk sintered silver and silver film cathodes, and further research with the former was abandoned in favor of the more economic silver film electrode.

The high cost of palladium foil anodes indicated that a new look at non-noble metals was required. Early IGT attempts to use sintered nickel powder, described elsewhere (11), indicated that severe corrosion problems existed. The most serious difficulty arises from direct contact of the anode with the oxygen from the cathode because of air leakage through the electrolyte. A second problem arises when the anode is operated at polarization conditions such that electrochemical consumption of the nickel is possible. At 600°C., this polarization value is about 200 millivolts below the hydrogen consumption potential. This phenomenon has been discussed recently in some detail by Broers (3) for nickel and iron electrodes, and by Bloch (1) for these and other electrode materials. The most recent IGT experiments with nickel metal electrodes and improved electrolyte structures have been operated at 500°C. over 1500 hours at current densities between 15 and 25 ma. per sq. cm., without serious nickel corrosion. The lower operating temperature alleviates the direct chemical corrosion problem, but reduces the polarization zone in which the anode can be safely operated.

In order to determine the effect of electrode structure on cell performance, a number of recent experiments with sintered fiber metal electrodes have been made. Typical results comparing sintered powder and fiber metal electrodes are shown in Figure 2. So far, performance of fiber metal electrodes seems inferior to that of the sintered powder types. However, the possibilities of fiber metal structures have been only superficially explored, and more extensive research is now in progress.

The conclusions concerning electrode development are:

▶ Hydrogen permeable palladium-silver metal foil electrodes can be used for long periods of time (over 7 months) without apparent deterioration.

▶ Thin film silver cathodes, at 600°C., are relatively stable and make excellent low-cost structures for the molten-carbonate type fuel cell.

▶ Thin film anode structures are unstable, becoming rapidly flooded in proportion to the current drain on the cell.

▶ Sintered powder nickel anodes can be operated for at least 1500 hours without appreciable corrosion under the proper conditions.

PASTE ELECTROLYTE DEVELOPMENT

In molten carbonate fuel cells, the electrolyte can exist: 1) as a free liquid between appropriate electrode structures; 2) contained in a presintered porous inert matrix; 3) mixed with an inert powder to form a pasty structure above the melting point of the carbonate mixture. Because of technological problems associated with sealing, stability, contacting, and fabrication techniques, the first two approaches have been abandoned in favor of the paste electrolyte.

Paste electrolytes for the molten carbonate fuel cells can be prepared by cold-pressing, hot-pressing, hot injection or extrusion, and other special techniques, some of which have been described in some detail by other workers (10). In this paper, only variations in cold-pressing techniques will be explored, since these constituted the bulk of the IGT effort.

Binary and ternary eutectics of sodium-lithium carbonates and sodium-lithium-potassium carbonates were used in all experiments. The ternary

eutectic melts at about 100°C. below the binary mixture, and thus allows the construction of lower temperature cells. Typical 1000-cycle cell resistivities of 9 and 7 ohm-cm. were obtained for 50 weight % mixtures of ternary carbonate in magnesium oxide at 500° and 600°C., respectively. Thirty weight % mixtures of binary carbonate eutectic exhibited cell resitivities in the neighborhood of 11 ohm-cm. at 600°C. For the most part, cell resistances were dependent only on electrolyte mixtures and not on the electrode structure employed.

The electrolyte matrix employed was determined by the anode structure. In the case of the hydrogen-permeable foil anodes, 30 weight % molten carbonate disks were prepared with 70% coarsely grained magnesium oxide as inert constituent. This cold-pressed disk had a density of 70% of the theoretical after firing. Denser electrolyte compositions showed better open-circuit potential, but under load they polarized more heavily than the 70% density disk. Thus, in the case of foil anodes, where reaction products must escape through the electrolyte via the cathode, densification of electrolyte would be detrimental.

With the sintered metal electrodes, especially those consisting of nonnoble metals, densification of the electrolyte is important and increases both lifetime and performance characteristics of the fuel cell. Initial experiments with nickel electrodes and 70% density paste electrolyte exhibited lifetimes of the order of 100 hours. By increasing the density of paste electrolyte to about 80% of the theoretical, IGT has achieved lifetimes of 1500 hours. Increasing electrolyte density also increases both the load and open circuit potential by about 200 millivolts. Electrolyte densification can be achieved by repeated crushing and grinding procedures if care is taken to avoid metallic contamination. Also, it is advantageous to increase the total carbonate content of the mixture by the use of small grained (less than 1 micron) magnesium oxide, which has a greater melt retention capacity.

Recent experiments, in which cold-pressed and fired disks are heated to within five degrees of the melting point of the carbonate eutectic and then hot-pressed at moderate pressures, indicate that disks with 96% of the theoretical density can be prepared.

The conclusions concerning paste electrolytes are:

▶ High-density electrolyte pastes are detrimental to the performance of fuel cells using hydrogen-permeable foil anodes.

▶ In all other cases high-density pastes are essential for achieving reasonable cell lifetimes.

▶ Cold-pressed disks can achieve a maximum density of about 85% by repetitive crushing and grinding techniques.

▶ Hot-pressing previously cold-pressed disks at a few degrees below the melting point causes significant densification to take place.

NATURAL GAS REFORMING

Four modes of operation are theoretically possible for natural gas utilization in a molten carbonate fuel cell system:

1) Direct electrochemical oxidation of methane.

2) In situ reforming of methane and steam on the anode, and electrochemical oxidation of the carbon monoxide and hydrogen thus formed.

3) In situ catalytic reforming of methane and steam in the anode chamber and electrochemical oxidation of the carbon monoxide and hydrogen thus formed.

4) External catalytic reforming of methane and steam, followed by electrochemical oxidation of hydrogen or hydrogen-carbon monoxide mixtures in the fuel cell.

Scheme 1 has been found unacceptable because of the electrochemical inertness of methane even at relatively high temperatures and the occurrence of carbon deposition when methane alone is present at these temperatures.

Scheme 2 is undesirable because the temperature required for the reforming (750°C.) is higher than that needed for electrochemical oxidation of hydrogen. This places an undesirable high operational temperature handicap on the fuel cell. Moreover, the presence of excess steam reduces the electrode performance (6). Finally, it is very difficult to design an electrode which is effective both as an electrochemical element and as a reforming catalyst.

Scheme 3 is relatively unexplored but would be characterized by the same drawbacks as Scheme 2, except that the electrode would not be required to function both electrochemically and as a reforming catalyst.

Scheme 4 has been adopted by IGT as the most feasible, since it permits separate optimization of fuel cell and reformer units. It permits accurate control of the composition of the input gas to the fuel cell and allows the cell to be operated effectively at substantially lower temperatures (between 500° and 600°C.). The lower operating temperatures for the fuel cell enhance electrode stability and the lifetimes of the materials of construction.

The drawback of separate fuel cell and reformer units is a reduction of the overall system efficiency in the case where the fuel cell is operated at a lower temperature than the reformer. Theoretically, this reduction can be shown to be about 10% for a reformer operating at 750°C. and a fuel cell operating at 500°C. The loss in efficiency for the dual temperature system arises from the unavailability of the low-quality waste heat of the fuel cell for supply of the heat of reaction for the reforming operation. In actual practice other losses might be incurred when two units are used because of the inefficiency of the heat transfer processes. However, since the 10% reduction figure quoted above is based on the comparison of maximum theoretical efficiencies for the two systems and since there is a large amount of unused low-quality heat (500°C.) in the dual-temperature model, it is more likely that an efficiency closer to the theoretical maximum can be achieved with this model.

The higher voltage efficiencies experimentally achieved with the reformed mixture more than compensate for the engineering and theoretical losses resulting from the dual system mode of operation. In Figure 3 a comparison is shown between the performances of a fuel cell at 500°C., supplied with externally reformed natural gas, and of a fuel cell at 750°C. with the equivalent methane-to-water ratio for in situ reforming. Also shown in this figure is the experimentally observed ratio of efficiencies of the two systems. This ratio was computed from the products of the experimental Faradaic efficiency and voltage efficiency of the two cells. Thermal inefficiency is not considered in this figure. It is significant that with external reforming, performance in terms of efficiency is almost 2.5 times greater at practical current densities.

Reformer design for natural gas is well known, and many excellent reforming catalysts are commercially available. The costs of these catalysts and the corresponding reformer units are only a small fraction of fuel cell hardware costs. The incorporation of the reformer into the natural gas fuel cell system is readily achieved.

It may be concluded that the use of external reforming with natural gas molten carbonate fuel cells seems justified on the basis of the improved experimental performance of this system over in situ reforming, as well as the more moderate operating temperatures it imposes on the fuel cell.

BATTERY DESIGN AND SCALEUP

The progress made in other areas of the molten carbonate fuel cell development indicated that some attention should be given to the problems associated with battery design and scaleup. The first step in the process was the assembly of a battery consisting of several small laboratory cells in series (Figure 4). No difficulties were encountered in this relatively simple transition, and next the more formidable problem of scaleup was attacked. The long-life performance of the silver film cathode and palladium-silver foil anode indicated that these particular compounds were the best adapted for scaleup techniques. The greatest problems were expected with increasing the size of the electrolyte disks from the 3-inch diameter laboratory disks to the 6-inch square dimensions chosen for the battery development program. In order to achieve the same electrolyte properties developed with the smaller cells a one million-pound press was required for the paste electrolyte fabrication. Special die fixtures were designed, and the larger electrolyte bodies were fabricated without difficulty.

Components for the new battery are shown in Figure 5, and a ten-cell battery built from the components is shown in Figure 6. The battery is assembled at room temperature and moderately tightened. It is then heated to 600°C., and the final sealing is accomplished when the paste electrolyte is in a semisolid state. The battery can now be thermally cycled between ambient and operating temperatures without damage or further adjustment. A 100% leak-tight assembly has not yet been achieved, but this represents only a slight loss in fuel efficiency. Complete sealing is anticipated in future designs.

As seen in Figure 5, the cathode compartment is open to the atmosphere. This design feature is essential for any practical molten carbonate fuel cell system. The mode of operation of the battery is a direct carryover from the laboratory models and is shown schematically in Figure 7. A portion of the incoming methane is burned directly in a burner underneath the fuel cell battery. Another portion of the methane is passed through activated carbon to remove sulfur compounds and, after steam addition, through the reformer containing commercial nickel catalyst.

The hot flue gas, containing excess air, carbon dioxide and water, rises by natural convection;in passing by the reformer, the flue gas drops in temperature to sustain the endothermic reforming reaction. The flue gas then enters the open cathode chambers, rises through the fuel cell, and supplies the oxygen and carbon dioxide needed to maintain the cathodic reaction. The water vapor in the flue gas has no adverse effect on the fuel cell reaction. To conserve fuel and carbon dioxide, the spent anode gases should be recycled to the burner.

Battery performance is shown in Figure 8. Faradaic efficiencies as high as 40% have been achieved in this apparatus although complete system efficiencies, as might be expected in such a small battery, are very low.

Some conclusions arrived at in battery design are:

▶ Operation of a multiple-cell battery molten carbonate fuel cell has been demonstrated.

▶ A mode of operation comprising a gas burner-reformer-open cathode fuel cell has been defined.

ECONOMIC EVALUATION

In order to evaluate the economics of a fuel cell system both its application and design must be considered. Von Fredersdorff (12) has outlined the economics of the domestic fuel cell application in considerable detail. In this section a brief description of the economics of fuel cell hardware as a function of its operating characteristics will be presented. The cost of fuel cell hardware depends on the cost of materials and cost of manufacturing.

Since manufacturing costs are difficult to estimate at this early stage of development, only the material costs for the most recent IGT design will be evaluated. The design model is similar to that described in the last section, with two significant changes. Nickel electrodes are used in place of the expensive silver-palladium foil and a parallel, dual element, geometry is chosen in place of the bipolar flange. The effect of this last change is to eliminate the flange completely from the fuel cell design, using the electrode itself as a structural element.

In Table II, the itemized cost of the various materials used in the IGT battery are given. These costs, plus the costs of fittings and an additional 10% of the total to cover miscellaneous materials, were used to compute the curves in Figure 9. In this figure battery material costs are plotted as a function of current density at constant voltage for various single-cell potentials. The dashed line represents the IGT fuel cell performance curve. Since fully manufactured batteries at $300 per kilowatt are reasonable for domestic fuel cell applications, an increase in cell performance by a factor of about two is necessary.

It may be concluded that only moderate improvements in voltage-current characteristics of the molten carbonate fuel cells are required to bring them within the economic framework of domestic applications.

<div align="center">ACKNOWLEDGMENT</div>

<div align="center">LITERATURE CITED</div>

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      "High Temperature Methane Fuel Cells," in Young, G. J., ed., "Fuel
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      Fuel Cell System," in Young, G. J., ed., "Fuel Cells," Vol. II, 50-67.
      New York: Reinhold Publ. Corp. (1963).

Table I.-PERFORMANCE OF POROUS NOBLE METAL ANODE FILMS

Anode Material	Preparation Method	Performance Decay,* hr.		Cell Lifetime, hr.
		90%	75%	
Pt	Paint	15	85	108
Ag-Pt	Paint	4	17	41
Pt	Paint	40	57	66
Pd	Paint	26	60	138
Pd	Paint	17	42	95
Pd	Paint	15	45	72
Pd	Vacuum Deposited	100	Not Determined	293

* Time to reach 90% and 75% of initial performance

Table II.-FUEL CELL HARDWARE COSTS

Material	Cost
Electrolyte paste - 100 mil thick ($MgO-Na_2CO_3-K_2CO_3-Li_2CO_3$)	$ 0.37/sq. ft.
Nickel anode - 25 mil thick	0.14/sq. ft.
Silver cathode - 0.4 mil thick	0.43/sq. ft.
Carbon steel anode current collector - 18 GA.	0.16/sq. ft.
Stainless steel cathode current collector - 18 GA.	1.18/sq. ft.
Stainless steel frame - 125 mil thick	0.14/ft.
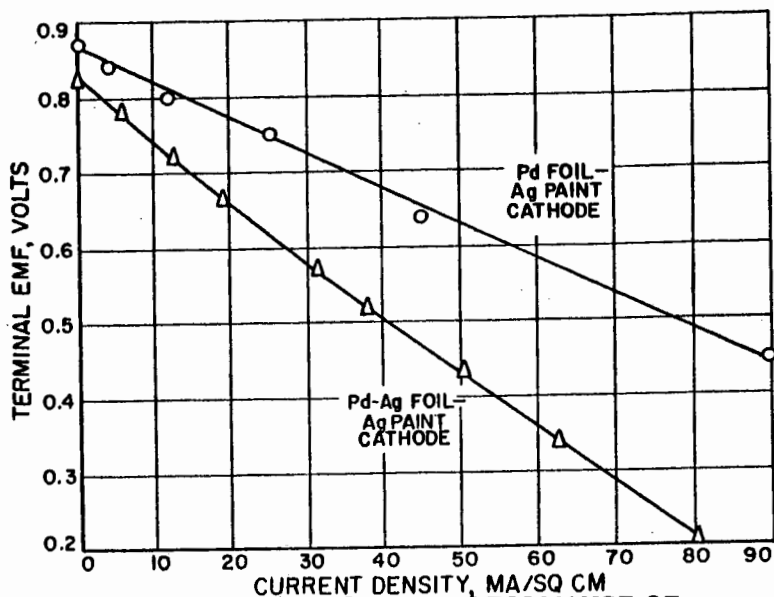
Fig. 1.--COMPARISON OF PERFORMANCE OF
PURE PALLADIUM AND PALLADIUM-SILVER ANODE
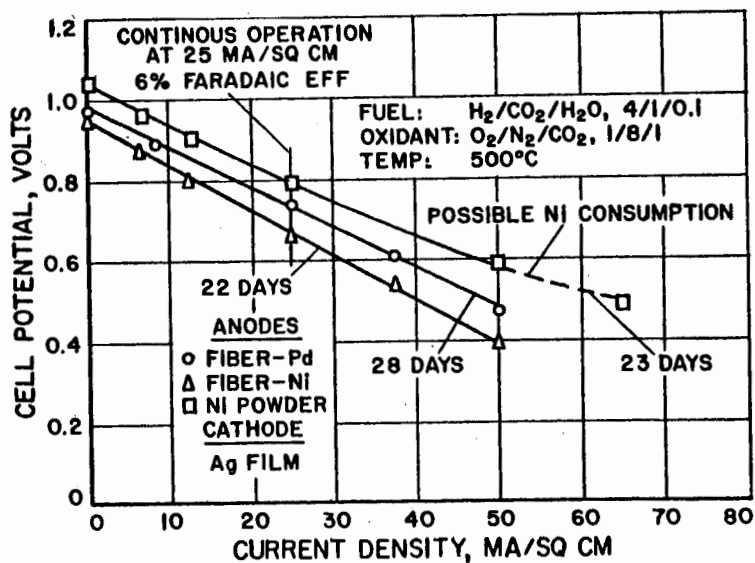HIGH-TEMPERATURE FUEL CELLS AT 600° C

Fig. 2.--EFFECT OF DIFFERENT ANODES ON
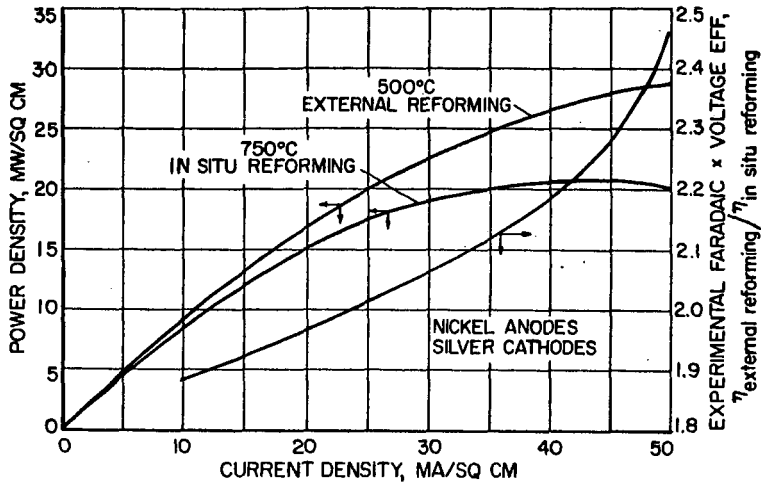HIGH-TEMPERATURE FUEL CELL PERFORMANCE

Fig. 3.- COMPARISON BETWEEN EXTERNAL AND
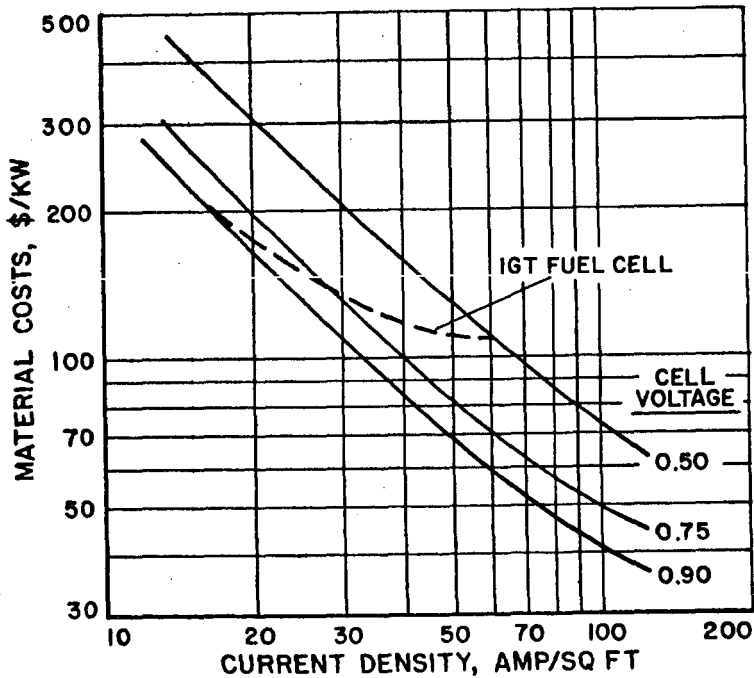IN SITU REFORMING ON FUEL CELL PERFORMANCE

Fig. 9.- ECONOMICS OF IGT HIGH-TEMPERATURE
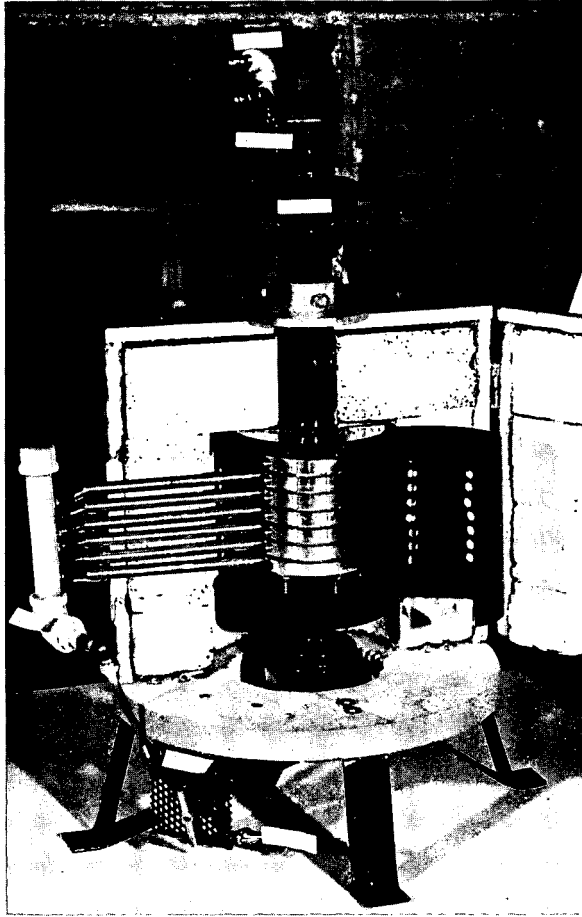MOLTEN CARBONATE FUEL CELL FOR
CONSTANT BATTERY VOLTAGE

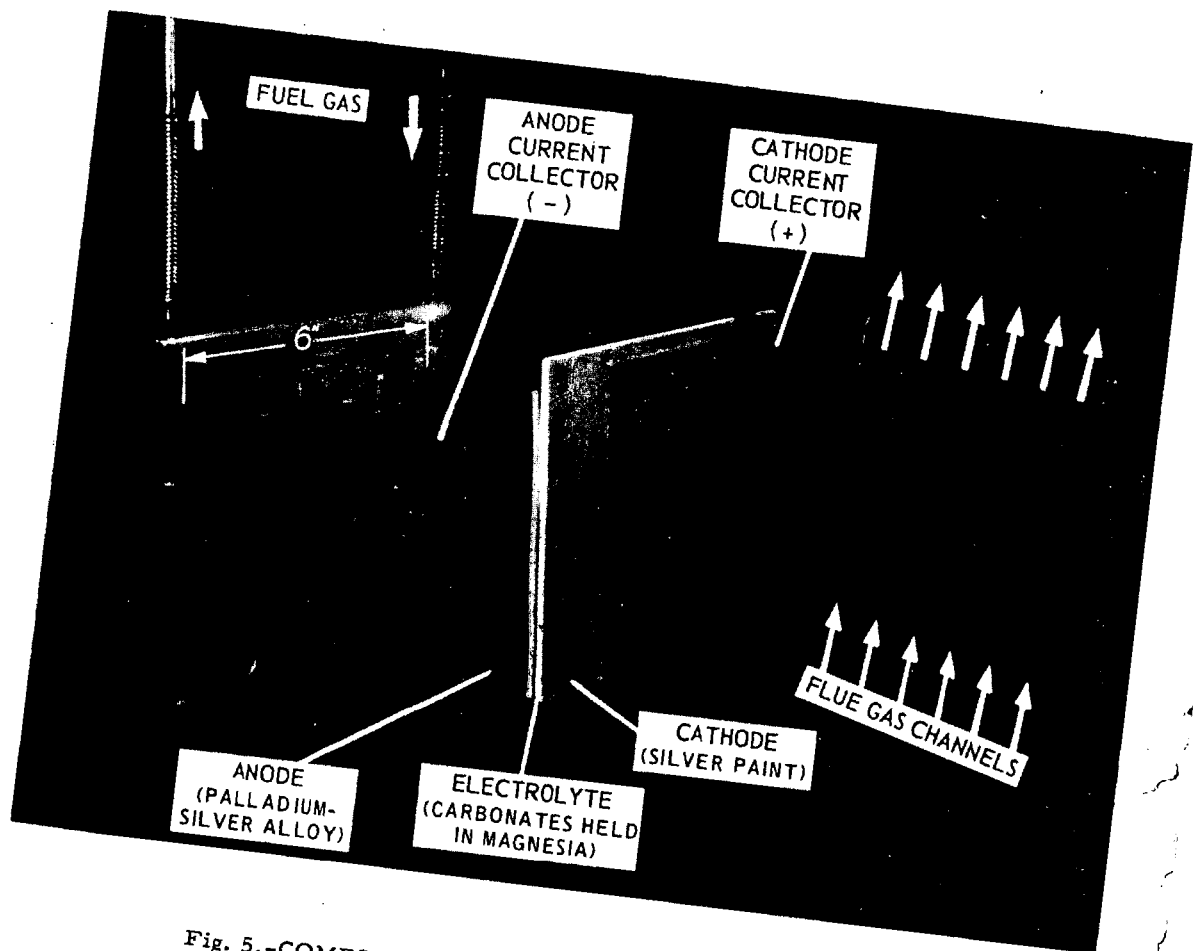Fig. 4.-LABORATORY SIZE IGT HIGH-TEMPERATURE
FUEL CELL BATTERY

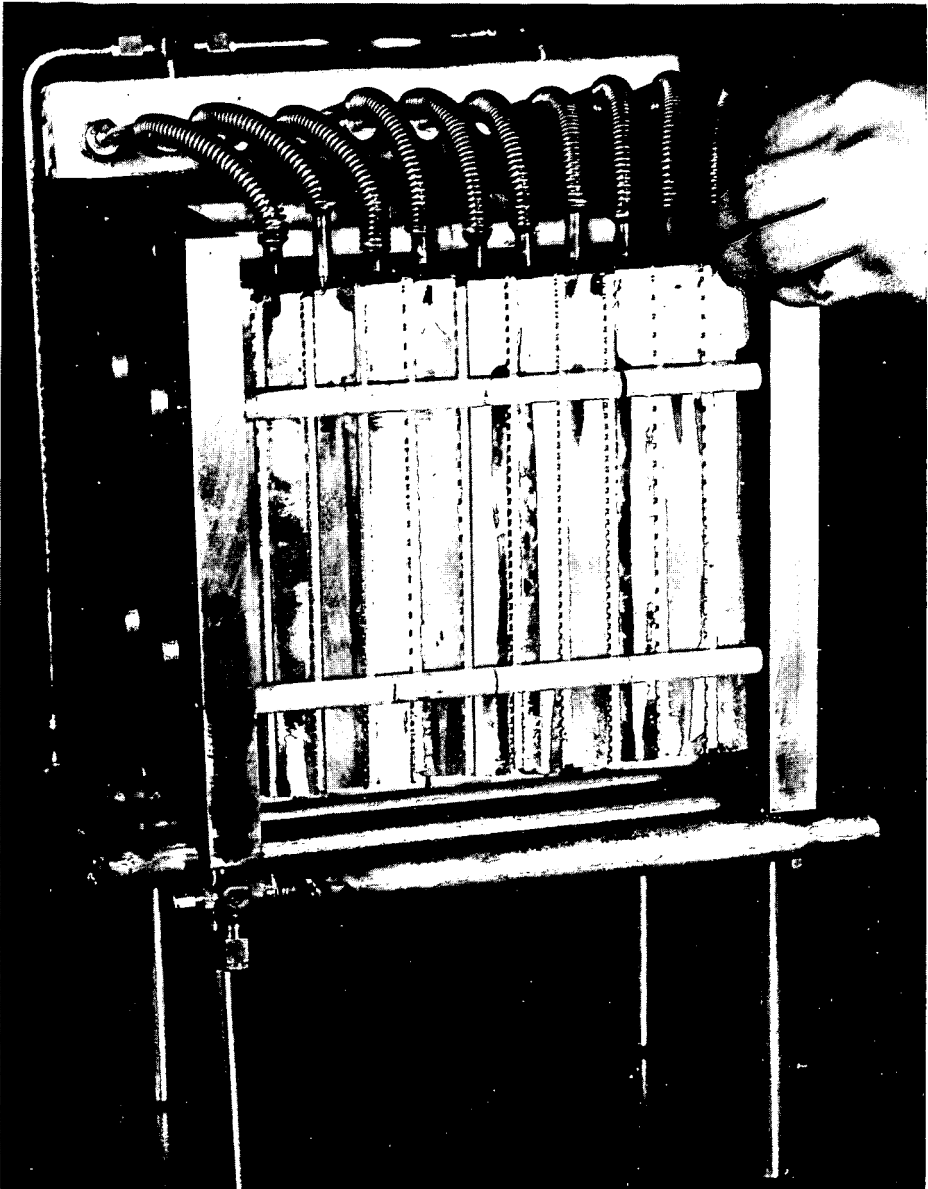Fig. 5.–COMPONENTS USED IN CONSTRUCTION OF SCALED-UP IGT FUEL CELL BATTERY

Fig. 6.-IGT HIGH-TEMPERATURE FUEL CELL BATTERY
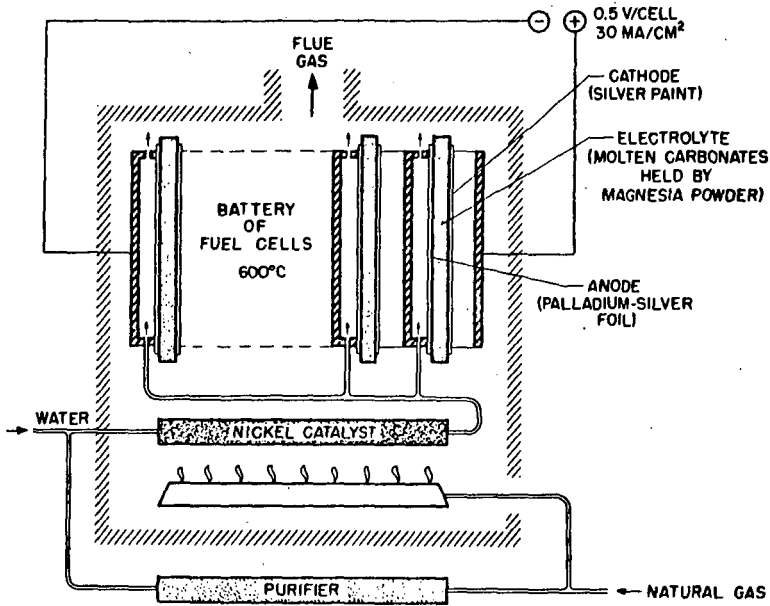AND REFORMER

Fig. 7.-SCHEMATIC REPRESENTATION OF
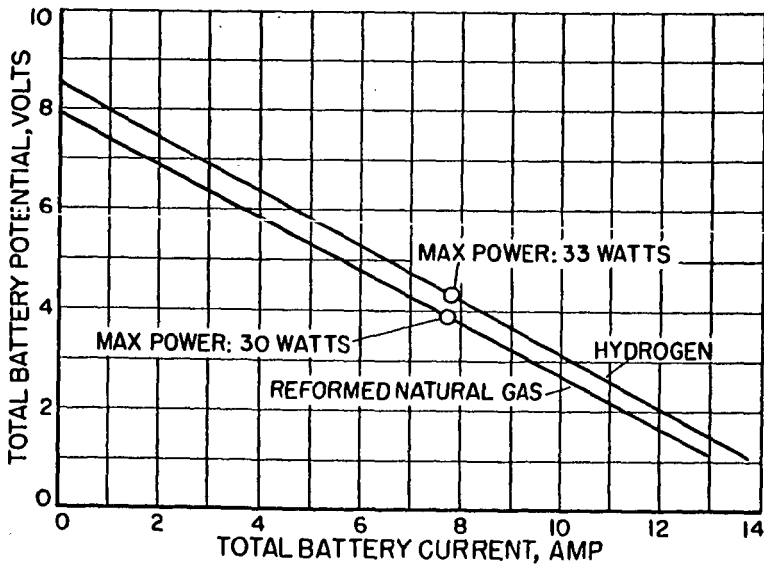IGT HIGH-TEMPERATURE NATURAL GAS FUEL CELL SYSTEM

Fig. 8.-PERFORMANCE OF 10-CELL HIGH-TEMPERATURE
FUEL CELL BATTERY